

## SUPPORTING INFORMATION

### **Phototriggered Supramolecular Polymerization of A [c2]Daisy Chain Rotaxane**

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## 1. Experimental Section

### 1.1 General Methods and Details

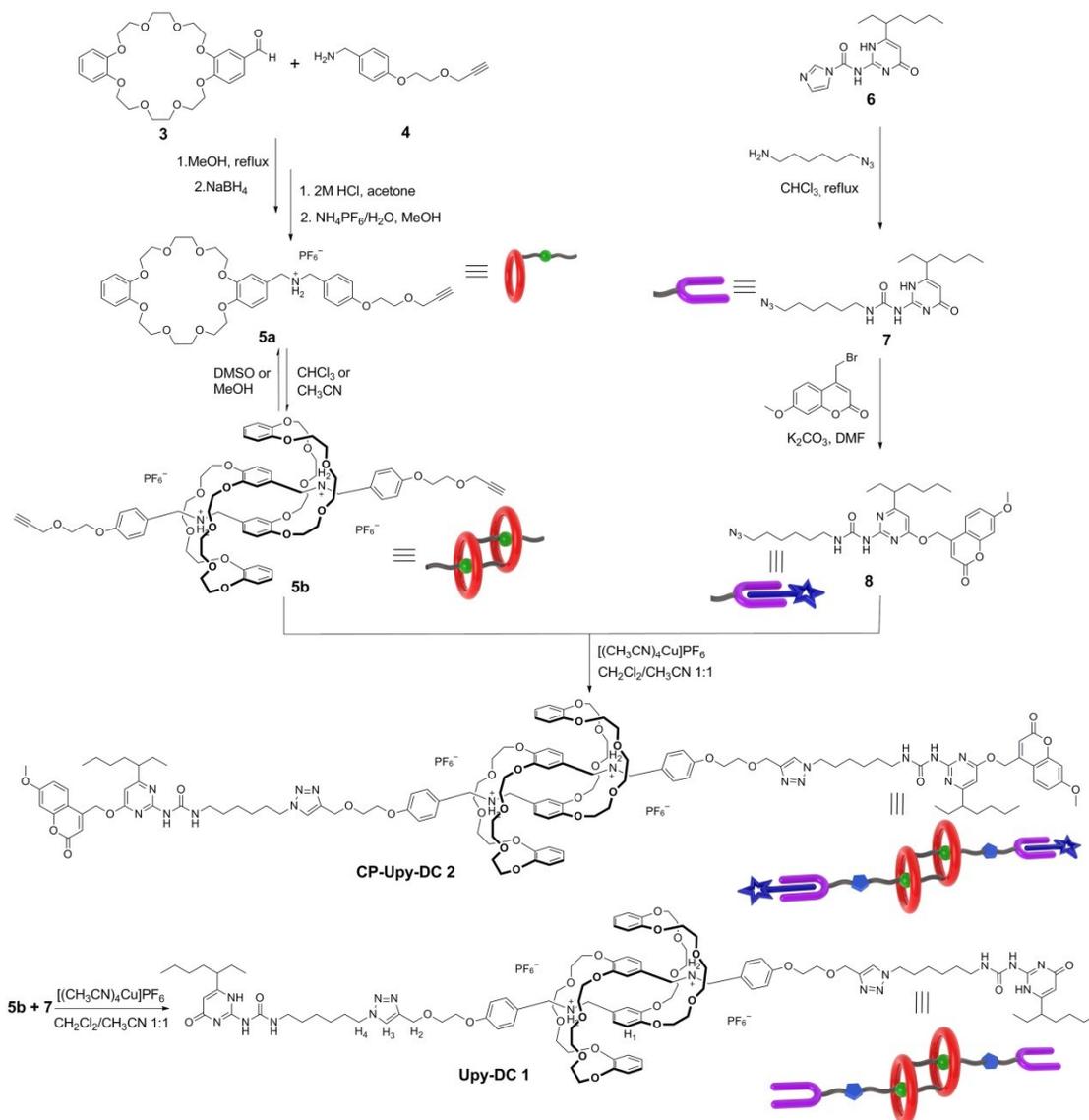
Chemicals were purchased from Acros, Aldrich, Fluka, Adamas, or Merck and used as received unless otherwise stated. Solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and 2D ROESY NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. Photo-controlled cleavage experiments were carried out with an UVATA UPF1 UV LED lamp (8 W/cm<sup>2</sup>) with a constant wavelength of 365 nm. HPLC measurements were carried out with Agilent 1100 (flow rate: 0.6 mL/min, eluent: methanol, detection wavelength: 272 nm). Viscosity measurements were carried out with Ubbelohde microdilution viscometers at 303 K in dichloromethane. DLS were measured on a MALV RN, ZETA SIZER, Model ZEN3600, 303K. AFM images were measured on a Solver P47-PRO, NT-MDT, and the samples were prepared by casting dilute solutions on freshly cleaved mica. TEM images were recorded on a JEOL JEM-1400 apparatus, and the samples were prepared by casting dilute solutions on a copper sheet. SEM images were obtained using a JSM-6360LV instrument, and the samples were prepared by casting dilute solutions on freshly cleaved mica.

### 1.2 Synthesis

Compound (2-formyl)dibenzo[24]crown-8 **3** was synthesized according to the procedure described by S. J. Cantrill, G. J. Youn, J. F. Stoddart<sup>1</sup> as a white solid. Compound **4** was synthesized according to our previously published methods.<sup>2</sup> Compound **6**<sup>3</sup> and Upy **9**<sup>4</sup> have been synthesized according to the literature procedures.

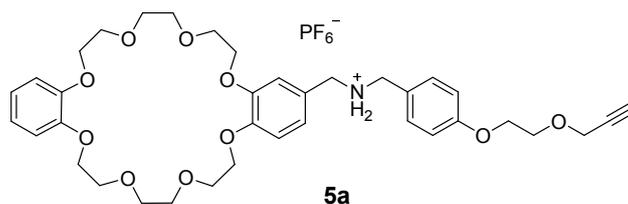
The synthetic route to Upy-DC **1** and CP-Upy-DC **2** are outlined in Scheme S1. A Schiff base was obtained by refluxing a solution of 1-formyl-dibenzo[24]crown-8 **4** and primary amine **4**. After reduction with NaBH<sub>4</sub>, followed by protonation with HCl and then counterion exchange with NH<sub>4</sub>PF<sub>6</sub>, the [c2]daisy chain precursor **5a** was obtained in yield exceeding 78%.  $^1\text{H}$  NMR spectra revealed that **5a** exist as monomers in polar solvents, such as [D<sub>6</sub>]DMSO (Figure S1a), with normal and the sharp  $^1\text{H}$  NMR signals. When the  $^1\text{H}$  NMR measurement was carried out in less polar solvents, such as [D<sub>3</sub>]acetonitrile, the self-assembled dimer **5b** became the major component.  $^1\text{H}$  NMR signals of the NH<sub>2</sub><sup>+</sup> protons and crown ether moiety are shifted and split, becoming much broader and more complicated.<sup>5,6</sup> The synthesis of coumarin caged Upy azide **8** was carried out in formamide dimethyl via etherification between 4-bromomethyl-7-

methoxy-coumarin and Upy azide **7**. Finally, **5b** was treated with **8** and **7** in dichloromethane/acetonitrile (1/1, v/v), respectively, via a “CuAAC click reaction” to afford **CP-Upy-DC 2** and **Upy-DC 1** successfully in yield exceeding 85% after purification by chromatography.



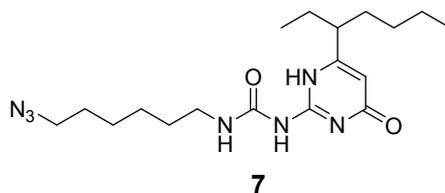
**Scheme S1.** Synthesis of the daisy chain rotaxane containing coumarin protected Upy terminals **CP-Upy-DC 2** and uncaged **Upy-DC 1**.

### 1.2.1 Synthesis of [c2]daisy chain precursor 5a



2-Formyldibenzo[24]crown-8 (1.0 g, 2.1 mmol) and amine **4** (0.48 g, 2.5 mmol) were dissolved in dry methanol (30 mL) and the mixture was heated under reflux in an argon atmosphere for 30 h. After cooling, NaBH<sub>4</sub> (0.40 g, 10 mmol) was added by portions at 0 °C. The mixture was stirred at room temperature for 5 h; then, 20 mL of water were slowly added to quench the reaction. Methanol was evaporated, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The combined organic phase was washed with H<sub>2</sub>O (2 × 20 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was diluted with acetone (50 mL) before HCl (2 mL) was added. The mixture was stirred for 1 h and concentrated under reduced pressure to give a colourless oil, the residue was redissolved in acetone (8 mL) quickly and cooled to 0 °C, yielding a white precipitate slowly. The precipitate was collected and washed with acetone (5 mL). Methanol was added dropwise to a solution of solid in water (50 mL) until all the solid was dissolved. Then, a saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (10 mL) was added. The mixture was stirred vigorously for 20 min. The reaction mixture was filtered, the precipitate was collected and washed with H<sub>2</sub>O to give the product **5a** (1.32g, 78%) as a white powder. <sup>1</sup>H NMR (400 MHz, DMSO, 298 K) δ (ppm): 8.96, (s, 2H), 7.39 (d, J = 9 Hz, 2H), 7.09 (s, 1H), 7.03-6.97 (m, 4H), 6.96-6.91 (m, 2H), 6.90-6.85 (m, 2H), 4.21 (d, J = 2 Hz, 2H), 4.15-4.11 (m, 2H), 4.10-4.00 (m, 12H), 3.82-3.73 (m, 10H), 3.66 (d, J = 3 Hz, 8H), 3.48 (t, J = 2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, DMSO, 298 K) δ (ppm): 158.90, 148.90, 148.41, 148.17, 131.54, 124.16, 123.74, 122.95, 121.13, 115.38, 114.53, 113.99, 113.95, 113.43, 80.14, 77.33, 70.43, 70.40, 69.14, 69.02, 68.81, 68.72, 68.65, 67.62, 66.89, 57.59, 49.67, 49.31. HRMS (ESI) (m/z): [M - PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>37</sub>H<sub>48</sub>NO<sub>10</sub> 666.3278, found 666.3275.

### 1.2.2 Synthesis of ureidopyrimidinone azide 7

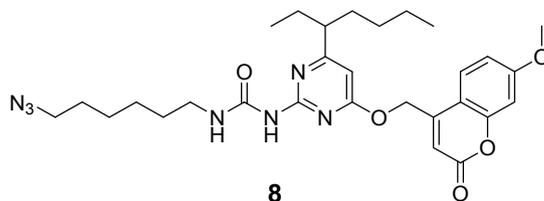


A solution of CDI activated isocytosine **6** (4.7 g, 16 mmol) and 6-azidohexan-1-amine (2.1 g, 15 mmol) in 50 mL of dry CHCl<sub>3</sub> was stirred at reflux overnight. After

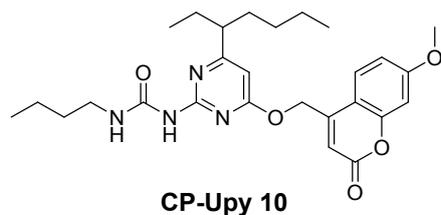
cooling,  $\text{CHCl}_3$  (30 mL) was added, and the organic layer was washed with 0.2 M HCl ( $2 \times 20$  mL), saturated aqueous  $\text{NaHCO}_3$  solution ( $2 \times 20$  mL) and brine ( $2 \times 20$  mL). The mixture was then dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed by evaporation under vacuum. The crude oil was purified by chromatography on a silica gel column ( $\text{CH}_2\text{Cl}_2/\text{Methanol}$  200/1) to give the ureidopyrimidinone azide **7** (7.8 g, 89%) as colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 13.24 (s, 1H), 11.92 (s, 1H), 10.24 (t,  $J = 5$  Hz, 1H), 5.81 (s, 1H), 3.22-3.29 (m, 4H), 2.25-2.35 (m, 1H), 1.49-1.73 (m, 8H), 1.36-1.45 (m, 4H), 1.19-1.33 (m, 4H), 0.84-0.92 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 167.89, 151.42, 150.18, 149.57, 100.93, 46.06, 40.05, 34.57, 27.59, 24.01, 23.95, 23.43, 21.31, 21.17, 21.06, 17.18, 8.60, 6.41. HRMS (ESI) (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_7\text{O}_2$  378.2617, found 378.2614.

### 1.2.3 Synthesis of coumarin-protected ureidopyrimidinone **8** and CP-Upy **10**

General Procedure A: Coumarin-protected Ureidopyrimidinone Formation. To a solution of ureidopyrimidinone (1 equiv.) and 4-bromomethyl-7-methoxy-2H-chromen-2-one (1 equiv) in 30 mL dry DMF,  $\text{K}_2\text{CO}_3$  (2 equiv) was added and the mixture was stirred at 90 °C overnight. The reaction mixture was concentrated under vacuum and 50 mL  $\text{CH}_2\text{Cl}_2$  was added. The organic layer was washed with brine ( $3 \times 20$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . The crude product was purified by chromatography on a silica gel column to afford the coumarin-protected ureidopyrimidinone **8** and CP-Upy **10**.



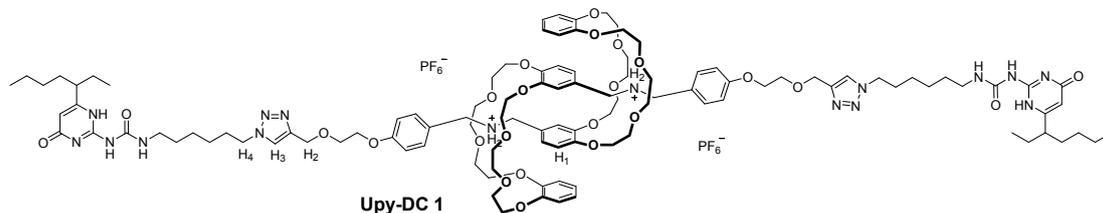
**8**: Ureidopyrimidinone azide **7** (1.0 g, 2.7 mmol) was treated according to General Procedure A. The crude product was purified by chromatography on a silica gel column (solvent gradient elution: petroleum ether/ $\text{CH}_2\text{Cl}_2$  from 2/1 to pure  $\text{CH}_2\text{Cl}_2$ ) to afford the coumarin-protected ureidopyrimidinone azide **8** in 67% yield as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 9.27 (s, 1H), 7.46 (d,  $J = 9$  Hz, 1H), 7.07 (s, 1H), 6.91 (dd,  $J = 9.2$  Hz, 1H), 6.88 (d,  $J = 2$  Hz, 1H), 6.39 (s, 1H), 6.27 (s, 1H), 5.50 (s, 2H), 3.90 (s, 3H), 3.39-3.31 (m, 2H), 3.26 (t,  $J = 7$  Hz, 2H), 2.50-2.41 (m, 1H), 1.68-1.56 (m, 8H), 1.45-1.38 (m, 4H), 1.34-1.10 (m, 4H), 0.90-0.80 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 174.90, 169.14, 162.92, 160.96, 157.47, 155.58, 154.27, 149.50, 124.36, 112.76, 110.60, 110.00, 101.26, 100.50, 62.91, 55.84, 51.37, 48.92, 39.79, 34.27, 29.76, 29.61, 28.81, 27.82, 26.68, 26.49, 22.78, 13.98, 12.04. HRMS (ESI) (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{29}\text{H}_{40}\text{N}_7\text{O}_5$  566.3091, found 566.3094.



**CP-Upy 10:** Ureidopyrimidinone **Upy 9** (1.0 g, 3.2 mmol) was treated according to General Procedure A. The crude product was purified by chromatography on a silica gel column (from petroleum ether/ $\text{CH}_2\text{Cl}_2$  2/1 to  $\text{CH}_2\text{Cl}_2$ ) to afford the coumarin-protected ureidopyrimidinone model compound **CP-Upy 10** in 73% yield as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 9.24 (s, 1H), 7.47 (d,  $J = 9$  Hz, 1H), 7.06 (s, 1H), 6.91 (dd,  $J = 9.2$  Hz, 1H), 6.88 (d,  $J = 2$  Hz, 1H), 6.40 (s, 1H), 6.27 (s, 1H), 5.49 (s, 2H), 3.90 (s, 3H), 3.39-3.31 (m, 2H), 2.50-2.41 (m, 1H), 1.72-1.52 (m, 6H), 1.48-1.38 (m, 2H), 1.34-1.23 (m, 4H), 0.95 (t,  $J = 7$  Hz, 3H), 0.90-0.80 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 174.97, 169.11, 162.91, 160.97, 157.52, 155.57, 154.32, 149.53, 124.38, 112.73, 110.62, 110.00, 101.26, 100.40, 62.88, 55.83, 48.97, 39.63, 34.23, 31.82, 29.62, 27.76, 22.76, 20.21, 13.97, 13.76, 12.03. HRMS (ESI) (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{37}\text{N}_4\text{O}_5$  497.2764, found 497.2767.

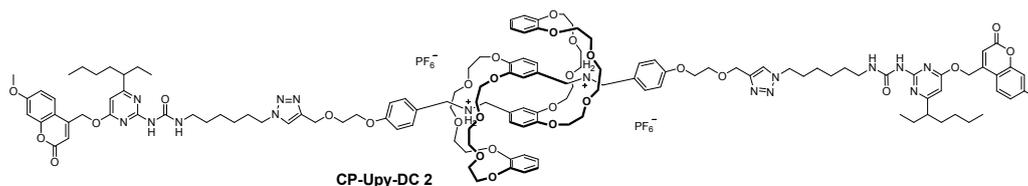
#### 1.2.4 Synthesis of Daisy Chain Rotaxane Upy-DC 1 and CP-Upy-DC 2

General Procedure B: Daisy Chain Rotaxane Formation. In a typical procedure, pseudorotaxane **5b** (1 equiv) and ureidopyrimidinone azide (3 equiv) were dissolved in dry  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (15 mL /15 mL). After stirred for 0.5 h,  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (10 equiv) was added, and the mixture was stirred at room temperature in a nitrogen atmosphere for 3 days. The solvent was removed under vacuum and the residue was purified by chromatography on a silica gel column to give the products **Upy-DC 1** and **CP-Upy-DC 2**.



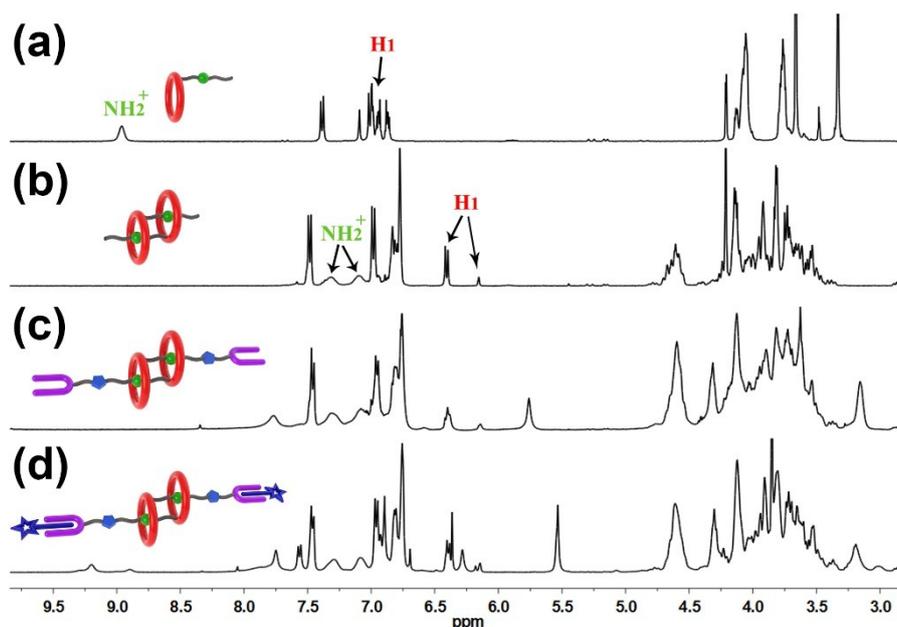
**Upy-DC 1.** Ureidopyrimidinone azide **7** (280 mg, 0.74 mmol) was treated according to General Procedure B. The crude product was purified by chromatography on a silica gel column ( $\text{CH}_2\text{Cl}_2/\text{Methanol}$ :100/1) to give the product **Upy-DC 1** in 89% yield as a foamed solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta$  (ppm): 13.15 (s, 2H), 11.83 (s, 2H), 10.14 (s, 2H), 7.73 (s, 2H), 7.46 (d,  $J = 8$  Hz, 4H), 7.28 (s, 2H), 7.09 (s, 2H), 6.95 (d,  $J = 8.4$  Hz, 4H), 6.86-6.70 (m, 12H), 6.41 (d,  $J = 8\text{Hz}$ , ~1.7H), 6.14 (s, ~0.3H), 5.76 (s, 2H), 4.70-4.52 (m, 12H), 4.31 (t,  $J = 6$  Hz, 4H), 4.26-3.40 (m, ~56H), 3.20-3.09 (m,

4H), 2.41-2.32 (m, 2H), 1.89-1.78 (m, 4H), 1.69-1.56 (m, 4H), 1.54-1.42 (m, 8H), 1.39-1.17 (m, 16H), 0.88-0.79 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta$  (ppm): 178.13, 164.80, 161.94, 161.19, 160.31, 153.12, 151.67, 151.46, 137.15, 136.14, 130.27, 129.77, 128.70, 128.07, 126.10, 120.16, 118.72, 117.24, 111.13, 77.10, 76.98, 75.97, 75.78, 75.60, 75.14, 74.96, 73.72, 73.05, 72.83, 72.69, 72.49, 69.31, 57.37, 57.04, 55.22, 50.05, 44.74, 37.96, 35.12, 34.25, 31.71, 31.23, 31.06, 27.56, 18.60, 16.31. HRMS (ESI) (m/z):  $[\text{M} - 2\text{PF}_6]^{2+}$  calcd for  $\text{C}_{110}\text{H}_{158}\text{N}_{16}\text{O}_{24}/2$  1044.0834, found 1044.0867.

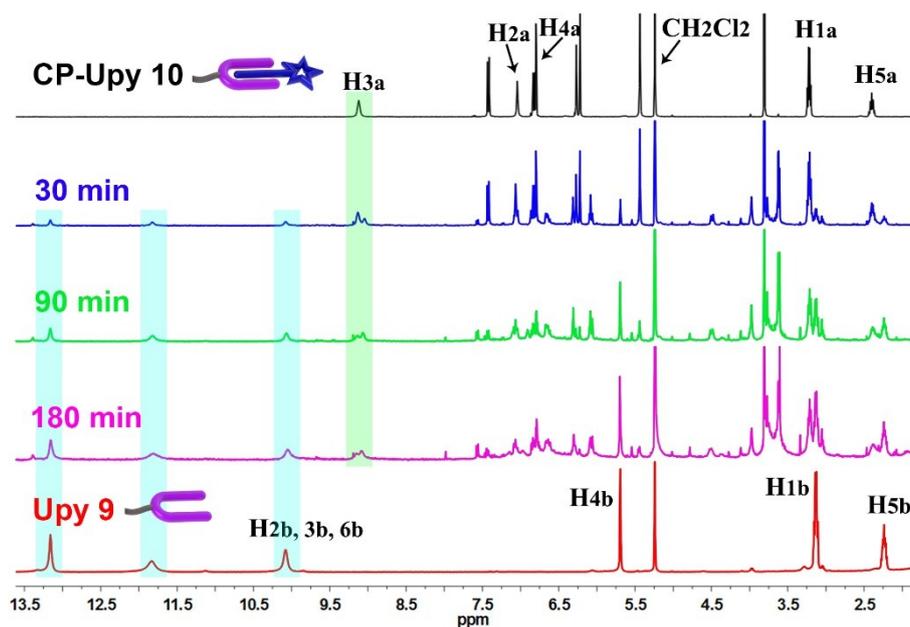


**CP-Upy-DC 2.** Coumarin-protected ureidopyrimidinone azide **8** (424 mg, 0.75 mmol) was treated according to General Procedure B. The crude product was purified by chromatography on a silica gel column ( $\text{CH}_2\text{Cl}_2/\text{Methanol}:100/1$ ) to give the solid product **CP-Upy-DC 2** in 85% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta$  (ppm): 9.18 (s, 2H), 7.82 (s, 2H), 7.71 (s, 2H), 7.57 (d,  $J = 9$  Hz, 2H), 7.46 (d,  $J = 9$  Hz, 4H), 7.28 (s, 2H), 7.09 (s, 2H), 6.96 (d,  $J = 9$  Hz, 4H), 6.94-6.90 (m, 4H), 6.88-6.72 (m, 12H), 6.39 (d,  $J = 8$  Hz,  $\sim 1.7\text{H}$ ), 6.36 (s, 2H), 6.28 (s, 2H), 6.14 (s,  $\sim 0.3\text{H}$ ), 5.54 (s, 4H), 4.70-4.51 (m, 12H), 4.30 (t,  $J = 7$  Hz, 4H), 4.24-3.40 (m, 62H), 3.23-3.16 (m, 4H), 2.54-2.45 (m, 2H), 1.86-1.78 (m, 4H), 1.66-1.56 (m, 8H), 1.51-1.43 (m, 4H), 1.39-1.20 (m, 16H), 0.84-0.75 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ , 298 K)  $\delta$  (ppm): 180.40, 174.64, 168.24, 165.76, 164.76, 163.15, 160.82, 155.44, 153.09, 151.63, 151.41, 136.10, 130.58, 130.23, 129.78, 128.06, 126.09, 120.13, 118.71, 117.48, 117.27, 117.22, 115.96, 115.16, 106.45, 105.49, 77.08, 76.94, 75.93, 75.80, 75.76, 75.11, 74.93, 73.69, 73.05, 72.82, 72.67, 72.44, 69.32, 68.48, 61.08, 57.36, 57.02, 55.15, 53.78, 44.67, 39.27, 36.65, 35.20, 34.72, 34.61, 32.87, 31.52, 31.18, 28.13, 27.78, 27.70, 18.75, 18.66, 16.62, 12.39. HRMS (ESI) (m/z):  $[\text{M} - 2\text{PF}_6]^{2+}$  calcd for  $\text{C}_{132}\text{H}_{174}\text{N}_{16}\text{O}_{30}/2$  1232.1308, found 1232.1329.

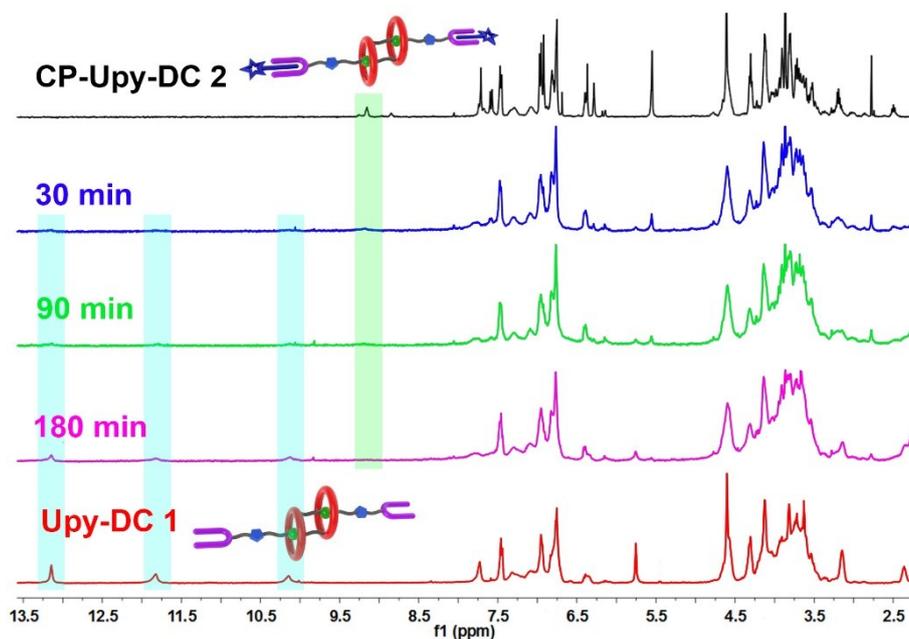
## 2. Supplementary Figures



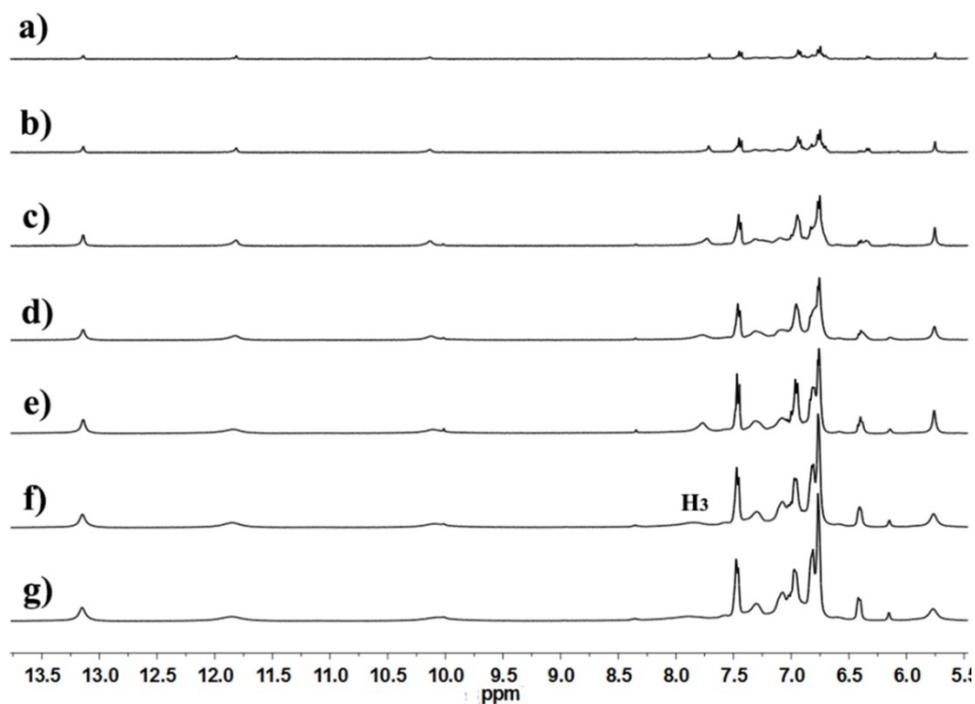
**Figure S1.**  $^1\text{H}$  NMR spectra of **5a** (400 MHz,  $[\text{D}_6]$ DMSO, room temperature), **5b**, **Upy-DC 1** and **CP-Upy-DC 2** (400 MHz,  $[\text{D}_3]$ acetonitrile, room temperature). Two sets of signals for the  $\text{NH}_2^+$  protons can be observed at  $\delta = 7.0 - 7.4$  ppm in **5b**, **Upy-DC 1** and **CP-Upy-DC 2**, indicating the formation of  $[\text{c}2]$ daisy chain structure.



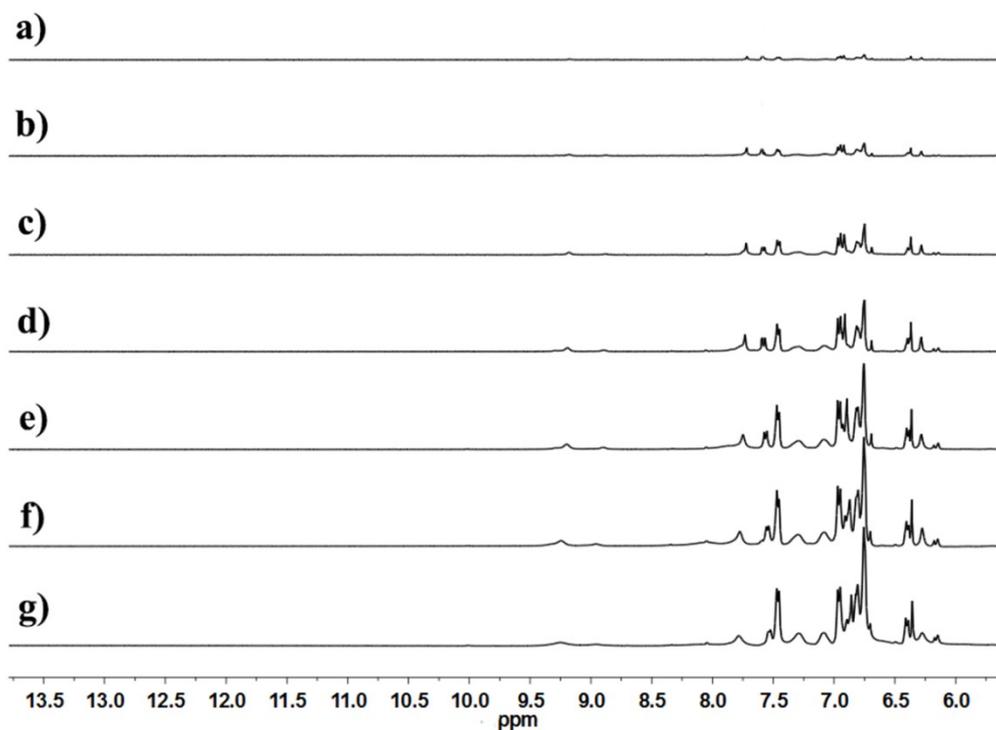
**Figure S2.**  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_2]$ dichloromethane, room temperature) of protected model compound **CP-Upy 10** at different irradiation times. The UV irradiation step was taken with 10 mM **CP-Upy 10** in a NMR tube. Under irradiation, **CP-Upy 10** gradually decomposed into photoproduct **Upy 9**. The coumarin moiety didn't cleave into a single photoproduct, probably due to the decomposition of the coumarin derivatives.



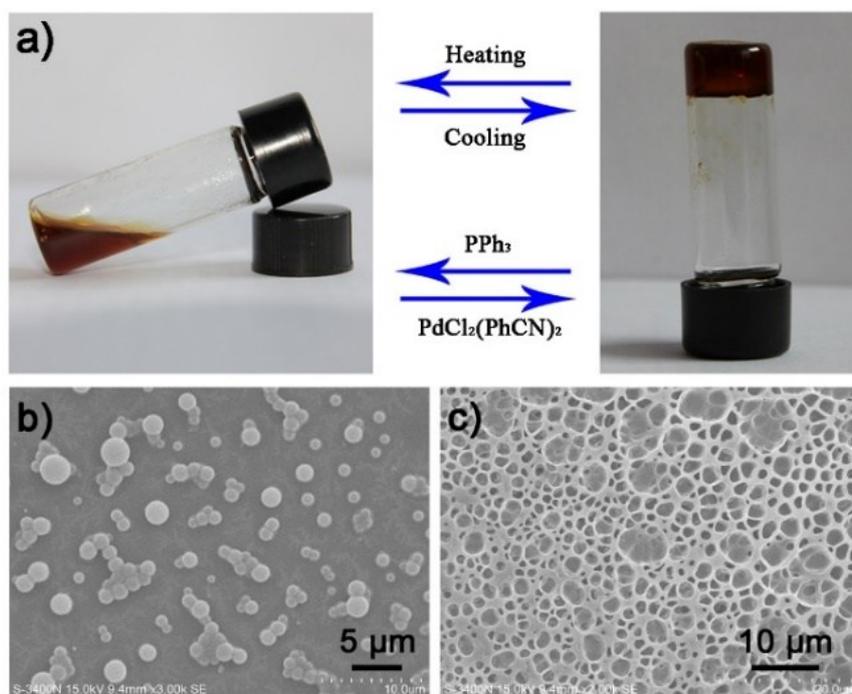
**Figure S3.**  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_3]$ acetonitrile, room temperature) of **CP-Upy-DC 2** at different irradiation times.



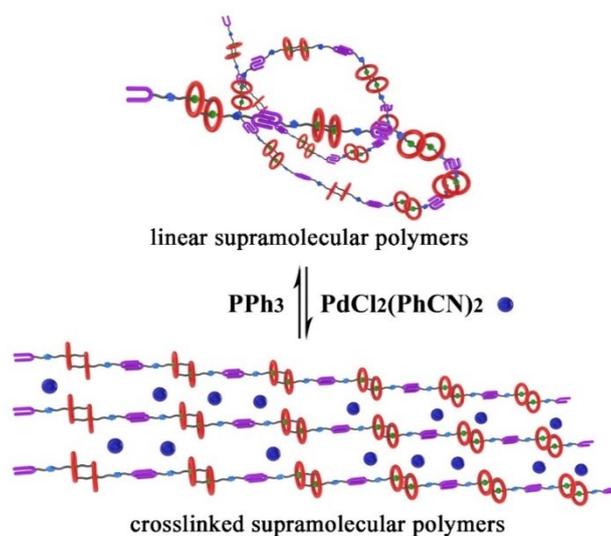
**Figure S4.** Partial  $^1\text{H}$  NMR spectra of monomer **Upy-DC 1** (400 MHz,  $[\text{D}_3]$ acetonitrile, room temperature) at various concentrations: a) 1 mM; b) 2 mM; c) 5mM; d) 10 mM; e) 20 mM; f) 40 mM; g) 60 mM.



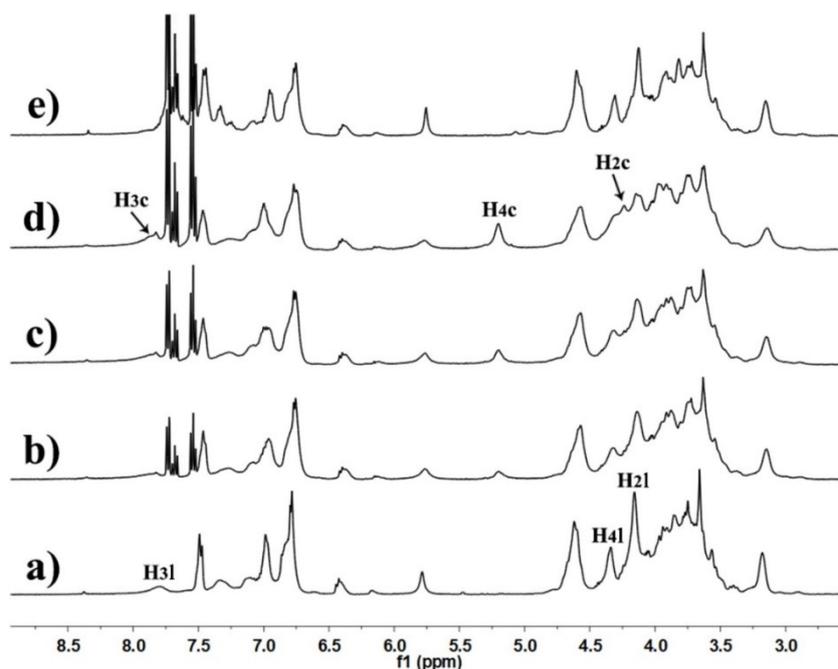
**Figure S5.** Partial  $^1\text{H}$  NMR spectra of monomer CP-Upy-DC 2 (400 MHz,  $[\text{D}_3]$ acetonitrile, room temperature) at various concentrations: a) 1 mM; b) 2 mM; c) 5 mM; d) 10 mM; e) 20 mM; f) 40 mM; g) 60 mM.



**Figure S6.** a) The reversible gel–sol transitions of the supramolecular polymer network gel (50 mM) triggered by thermo- and competitive ligand stimuli. b) SEM image of the linear supramolecular polymer (20 mM in acetonitrile); c) SEM image of the crosslinked supramolecular polymer (20 mM in acetonitrile).



**Figure S7.** Schematic representation of the reversible transition process between the linear and the crosslinked supramolecular polymers upon addition of  $\text{PdCl}_2(\text{PhCN})_2$  and  $\text{PPh}_3$ .



**Figure S8.** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_3]$ acetonitrile, room temperature) of 10 mM SSP upon progressive addition of  $\text{PdCl}_2(\text{PhCN})_2$  and  $\text{PPh}_3$ : (a) 0 equiv.; (b) 0.32 equiv.; (c) 0.59 equiv.; (d) 1.00 equiv. of  $\text{PdCl}_2(\text{PhCN})_2$ ; (e) 2.00 equiv. of  $\text{PPh}_3$  was added to (d) after filtration. Here “c” and “l” represent the cross-linked and linear species, respectively. As shown in (a)-(d), the resonance for the triazole proton  $\text{H}_3$  and adjacent protons  $\text{H}_{2,4}$  shift downfields while all signals become more broad, indicating the preferential coordination between triazole and  $\text{Pd}(\text{II})$  and subsequent formation of a crosslinked supramolecular polymer. Figure (e) shows the deconstruction of the supramolecular polymer network with the quantitative recovering of signals for the linear supramolecular polymers after  $\text{PPh}_3$  was put into the solution to competitively coordinate with  $\text{Pd}(\text{II})$ .

### 3. Calculation of Volume of half an Ellipsoid/ Diameter in solution

$$V = 1/2 * 4/3 * \pi * r^2 * h$$

Where r = radius from the AFM, h = height from AFM (in nm)

$$r = 150 \text{ nm}, h = 12 \text{ nm}$$

$$V = 0.5 * 1.333 * \pi * (150 * 150) * 12$$

$$V = 56 \times 10^4 \text{ nm}^3$$

$$\text{Volume of a sphere} = 4/3 * \pi * r^3$$

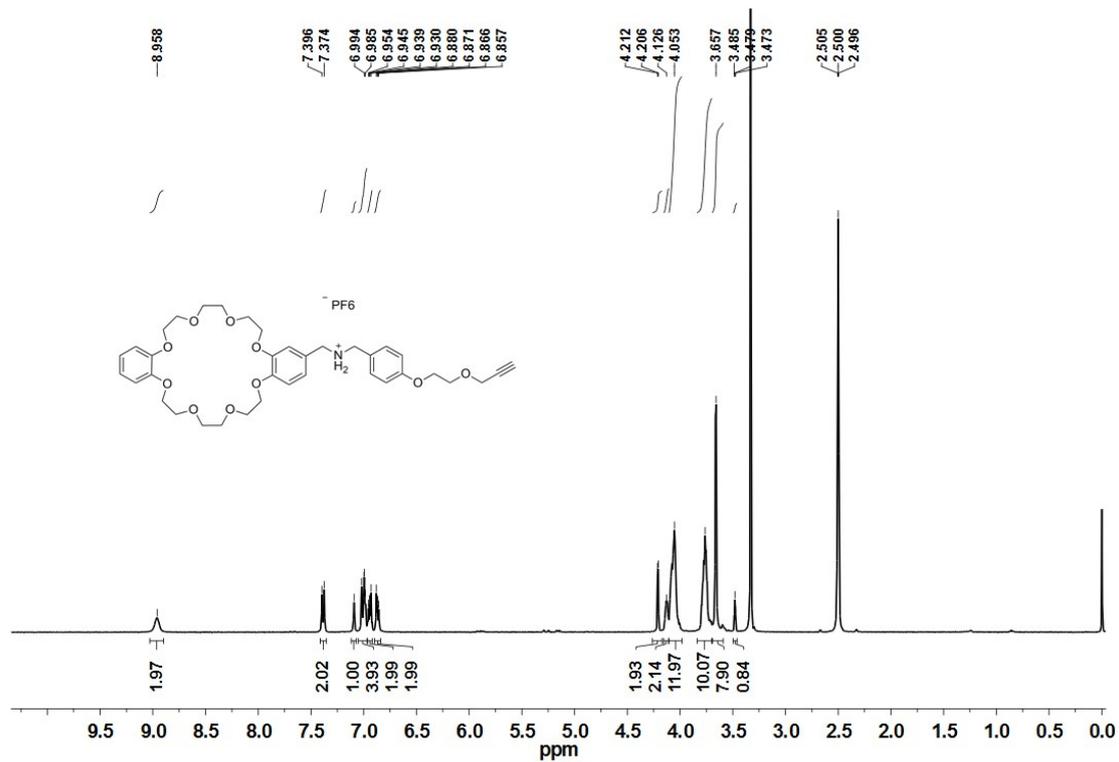
$$565059 = 4/3 * \pi * r^3$$

$$r = 51 \text{ nm (Radius of corresponding nanosphere)}$$

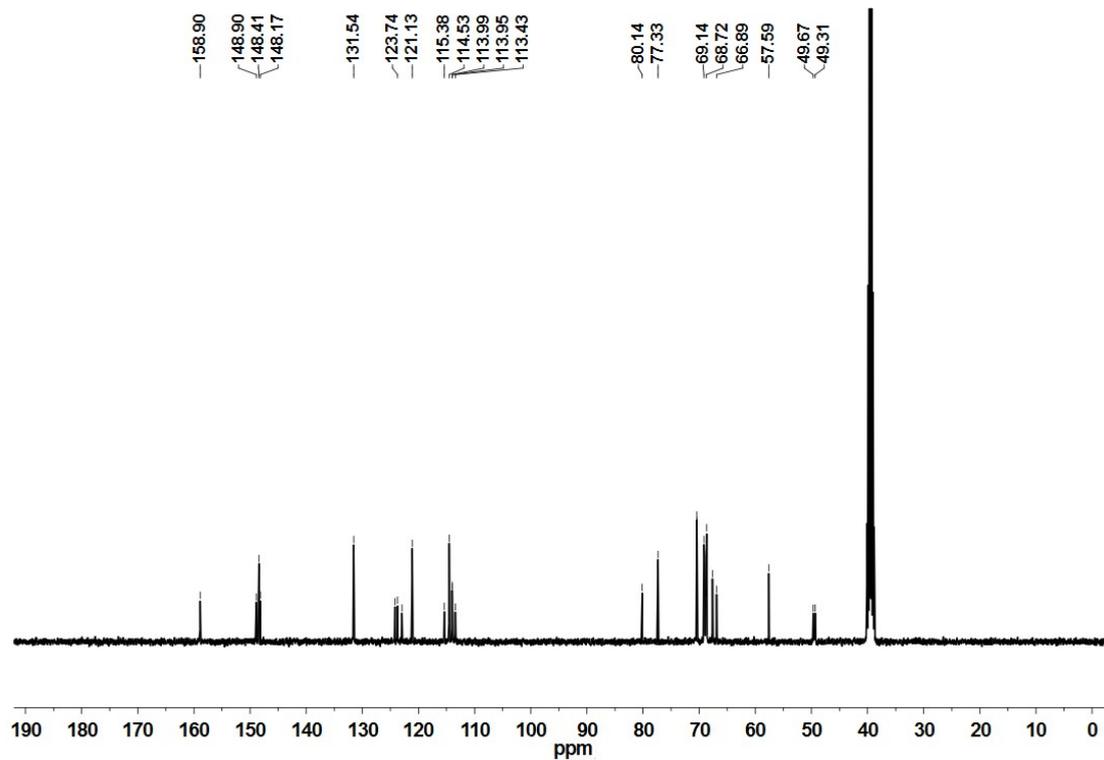
$$d = 102 \text{ nm (Diameter of corresponding nanosphere)}$$

## Reference

1. Cantrill, S. J.; Youn, G. J.; Stoddart, J. F.; Williams, D. J. *J. Org. Chem.* **2001**, *66*, 6857-6872.
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3. Keizer, H. M.; Gonzalez, J. J.; Segura, M.; Prados, P.; Sijbesma, R. P.; Meijer, E. W.; de Mendoza, J. *Chem. –Eur. J.* **2005**, *11*, 4602-4608.
4. Keizer, Henk M.; Sijbesma, Rint P.; Meijer, E. W. *Eur. J. Org. Chem.* **2004**, 2553-2555.
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<sup>1</sup>H NMR spectrum of 5a



<sup>13</sup>C NMR spectrum of 5a

## Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

161 formula(e) evaluated with 5 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-37 H: 0-100 N: 0-6 O: 0-10

QU-DH

ECUST institute of Fine Chem

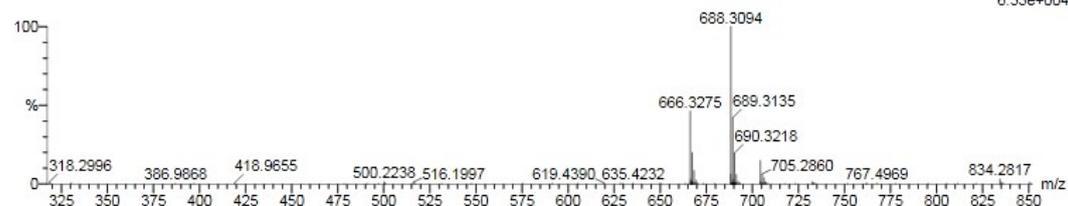
14-Mar-2014

19:30:16

1: TOF MS ES+

6.33e+004

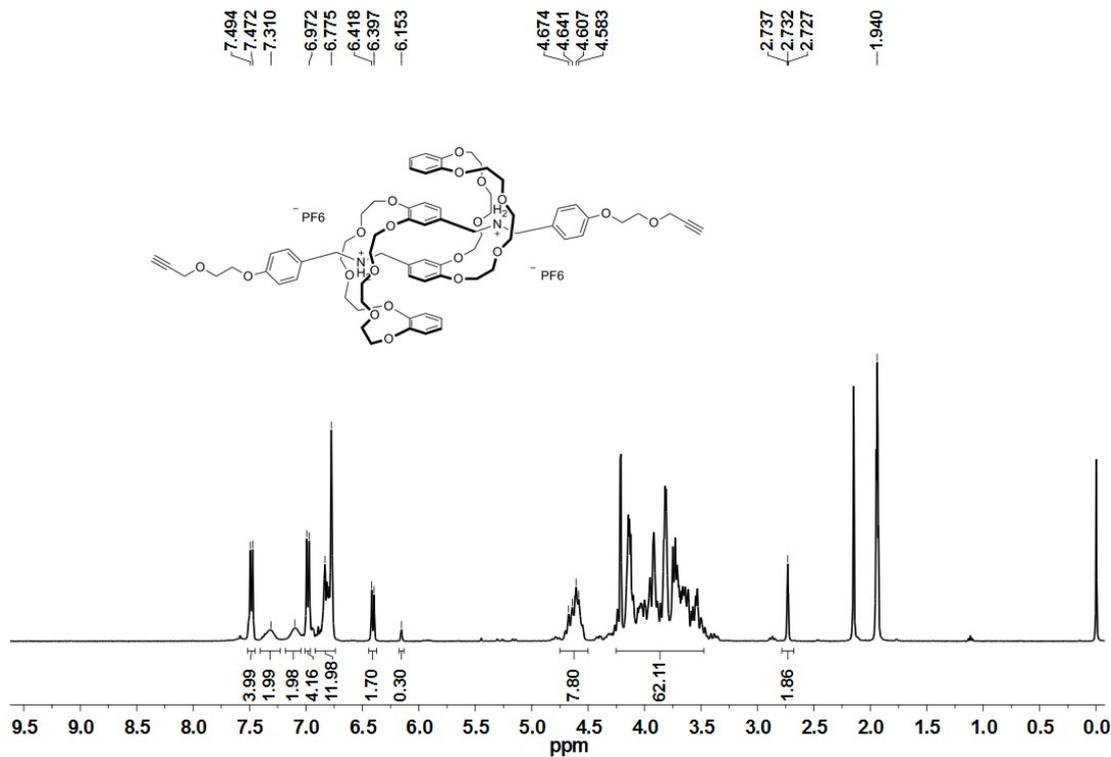
QDH-FX-1 193 (1.286) Cm (152.209)

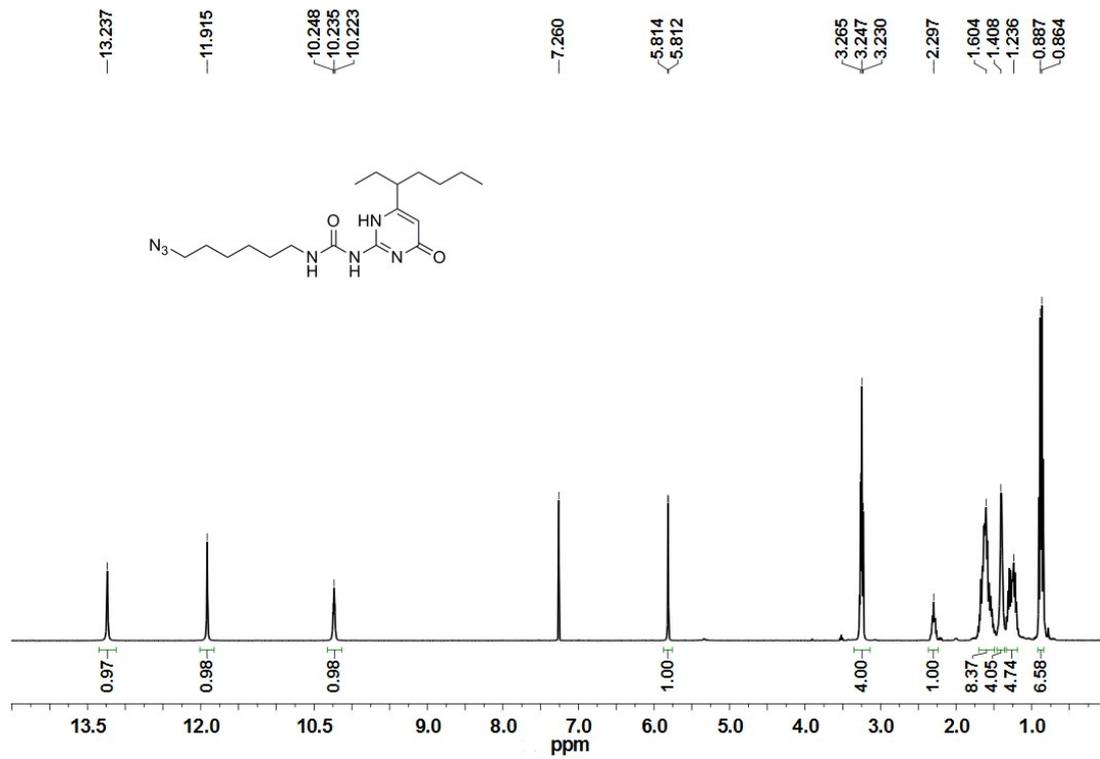


Minimum: -1.5  
 Maximum: 30.0 50.0 100.0

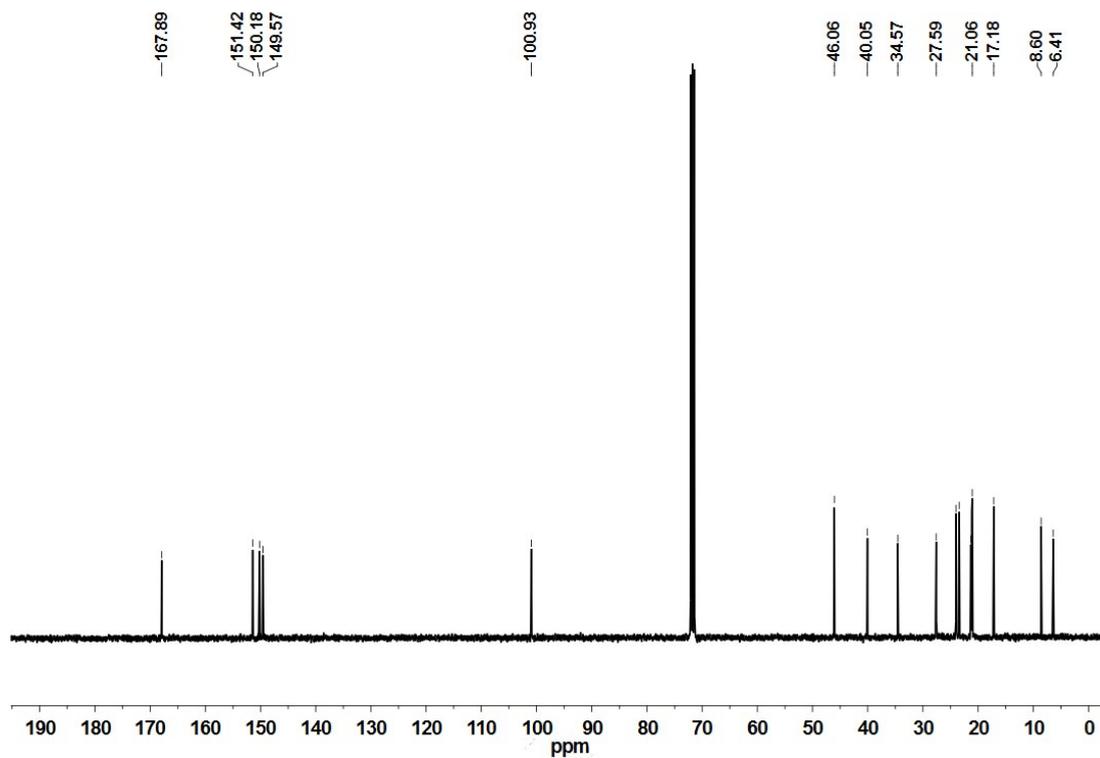
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
666.3275	666.3278	-0.3	-0.5	14.5	102.8	0.0	C37 H48 N O10

## ESI-Mass spectrum of 5a

<sup>1</sup>H NMR spectrum of 5b



<sup>1</sup>H NMR spectrum of 7



<sup>13</sup>C NMR spectrum of 7

Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

530 formula(e) evaluated with 19 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-50 H: 0-71 N: 0-7 O: 0-20

DH-QU

ECUST institute of Fine Chem

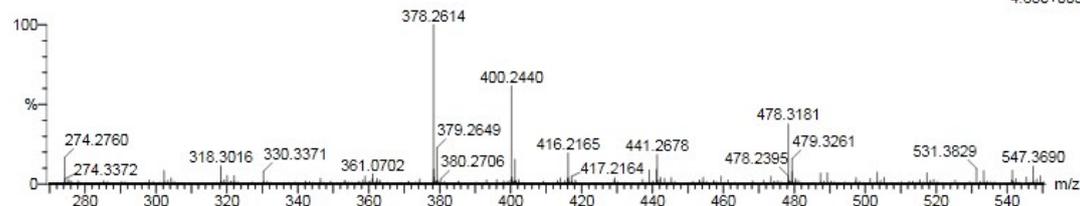
10-Mar-2014

22:16:14

1: TOF MS ES+

4.85e+003

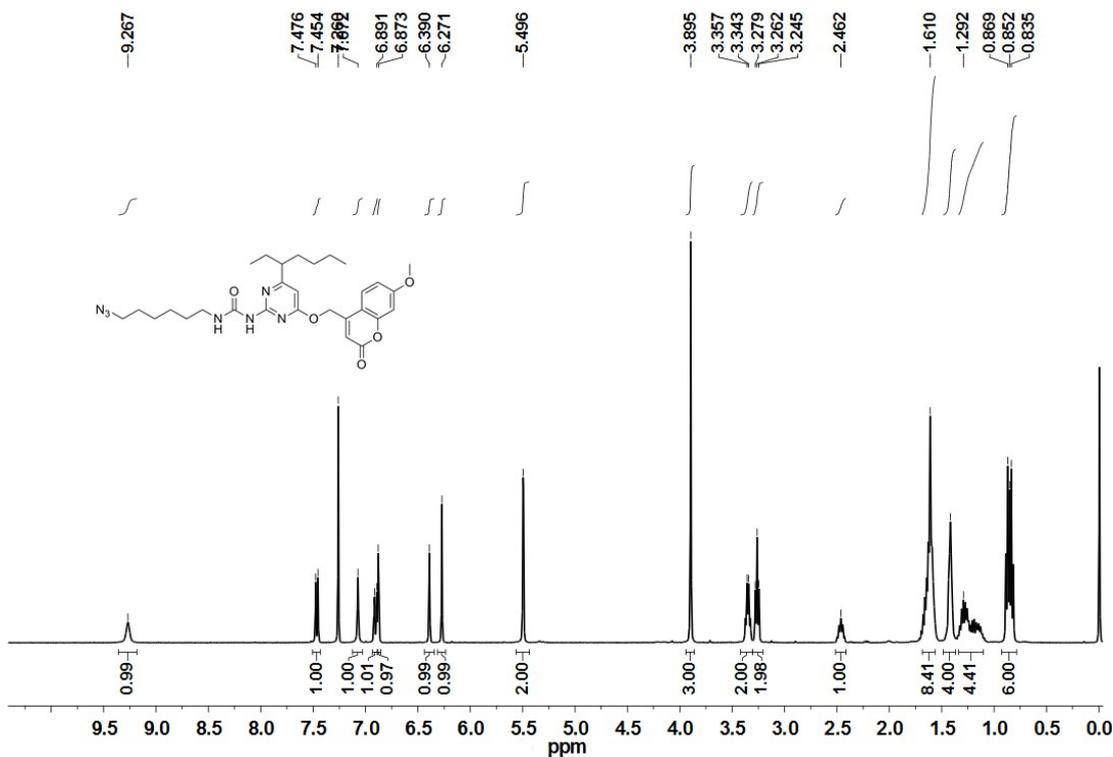
QDH-FX-1 220 (1.453) Cm (219.232)



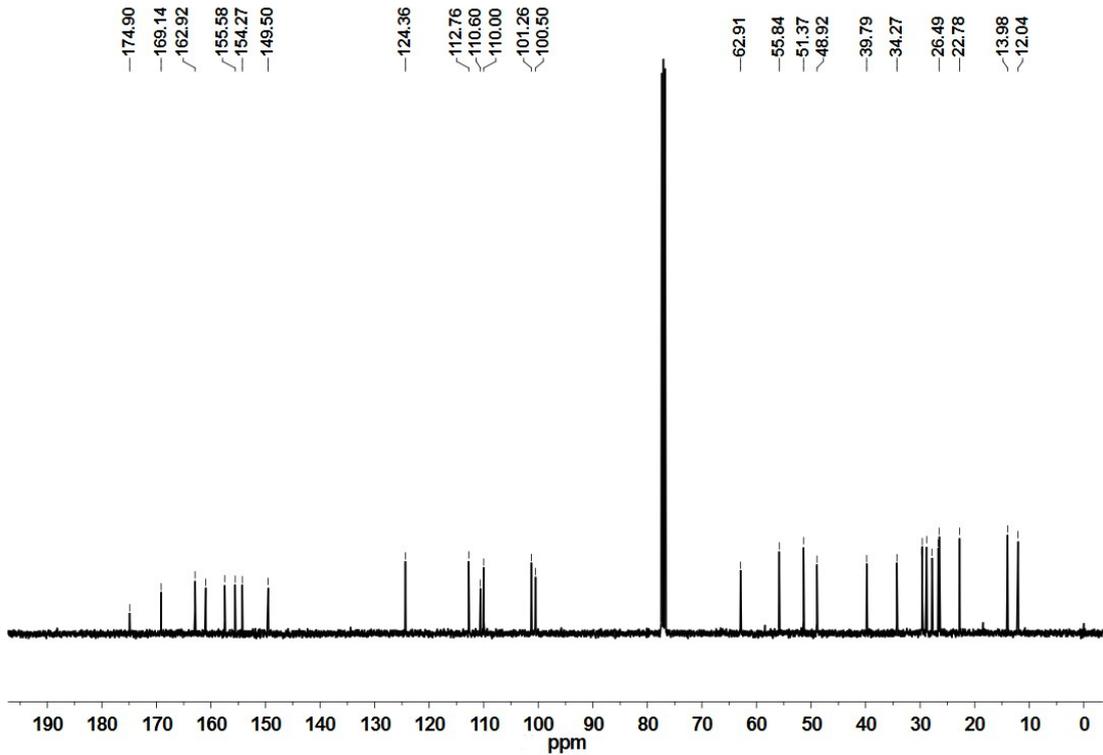
Minimum: -1.5  
 Maximum: 30.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
378.2614	378.2617	-0.3	-0.8	6.5	230.3	0.0	C18 H32 N7 O2

ESI-Mass spectrum of 7



<sup>1</sup>H NMR spectrum of 8



<sup>13</sup>C NMR spectrum of **8**

**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

503 formula(e) evaluated with 33 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-55 H: 0-57 N: 0-7 O: 0-12

DH-QU

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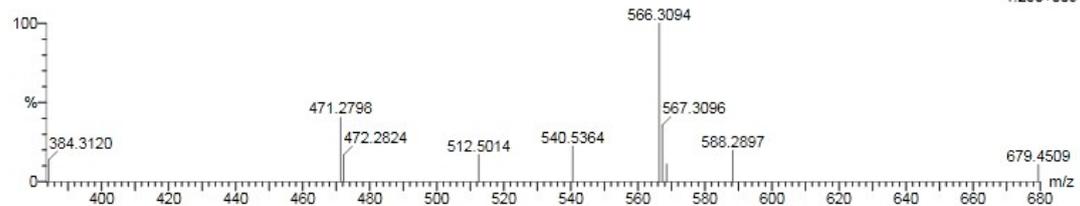
25-Feb-2014

21:42:10

1: TOF MS ES+

1.25e+003

QD-FX-1 25 (0.865) Cm (25:31)

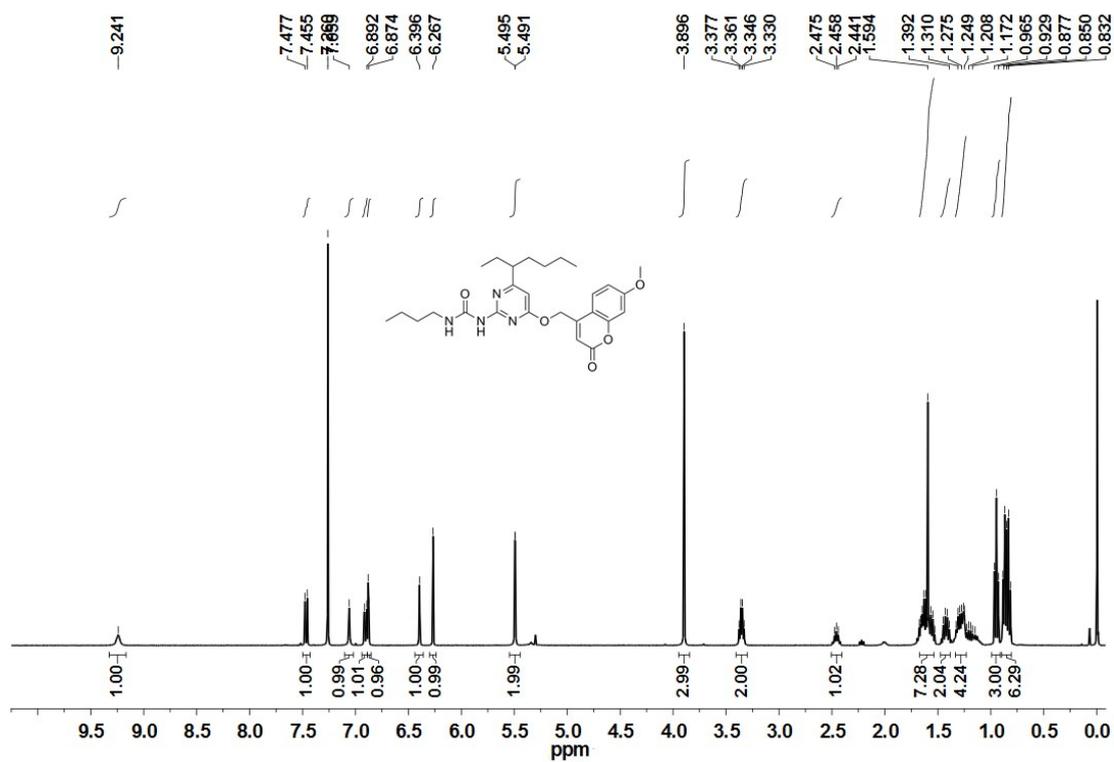


Minimum:

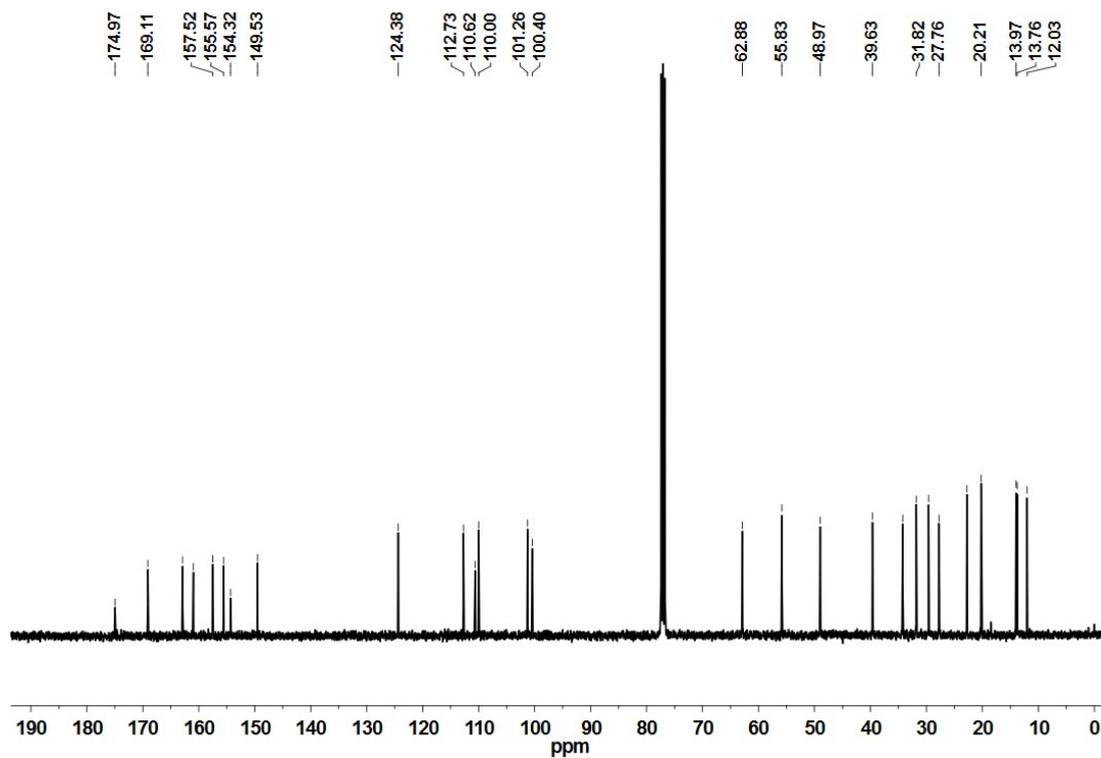
Maximum: 30.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
566.3094	566.3091	0.3	0.5	13.5	8.2	0.0	C29 H40 N7 O5

ESI-Mass spectrum of **8**



<sup>1</sup>H NMR spectrum of CP-Upy 10



<sup>13</sup>C NMR spectrum of CP-Upy 10

Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

118 formula(e) evaluated with 9 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-35 H: 0-50 N: 0-5 O: 0-5

DH-QU

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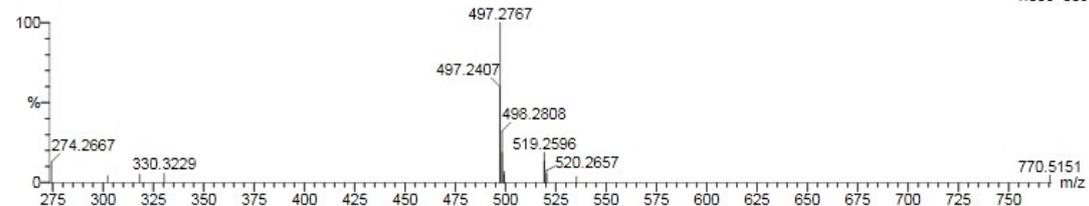
11-Jan-2014

13:48:05

1: TOF MS ES+

1.05e+003

QD-FX-4 13 (0.497) Cm (11:17)

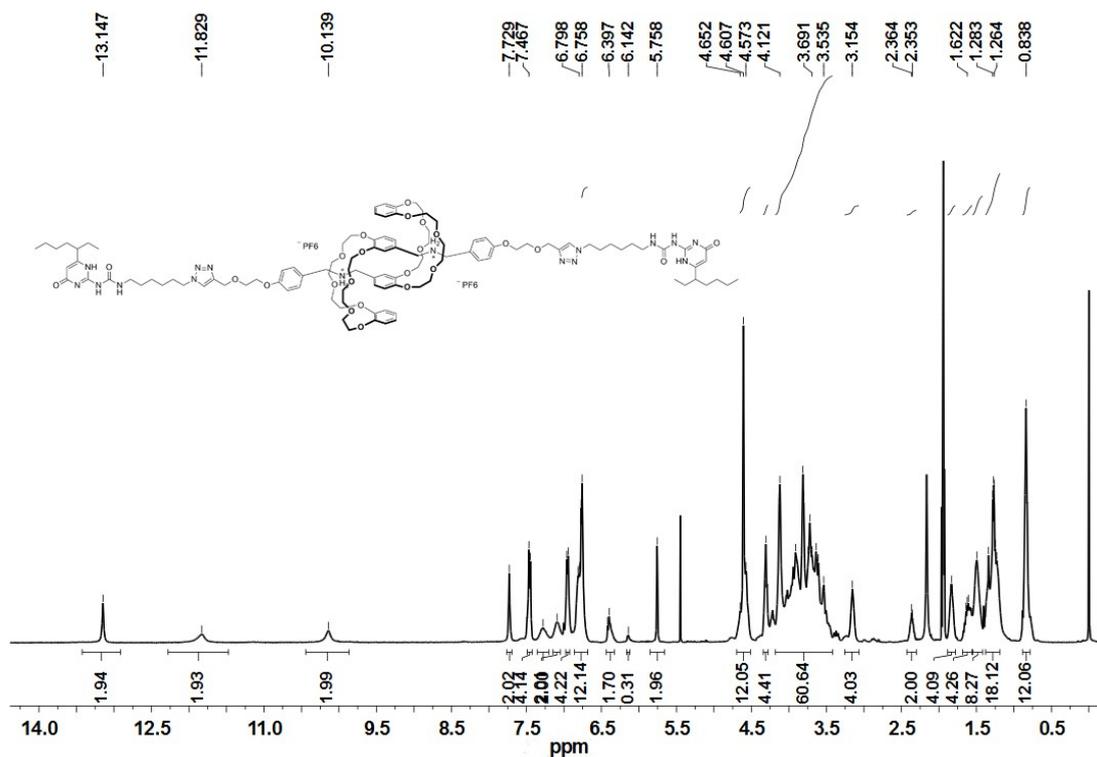


Minimum:

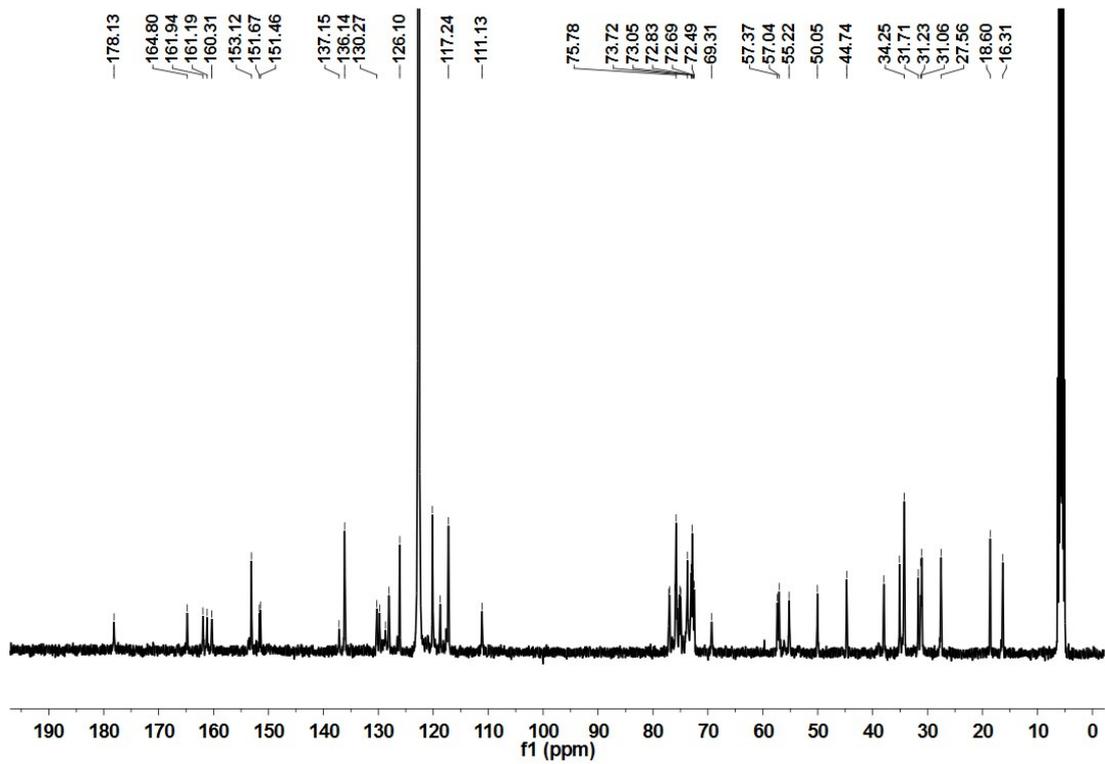
Maximum: 30.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
497.2767	497.2764	0.3	0.6	11.5	18.0	0.0	C27 H37 N4 O5

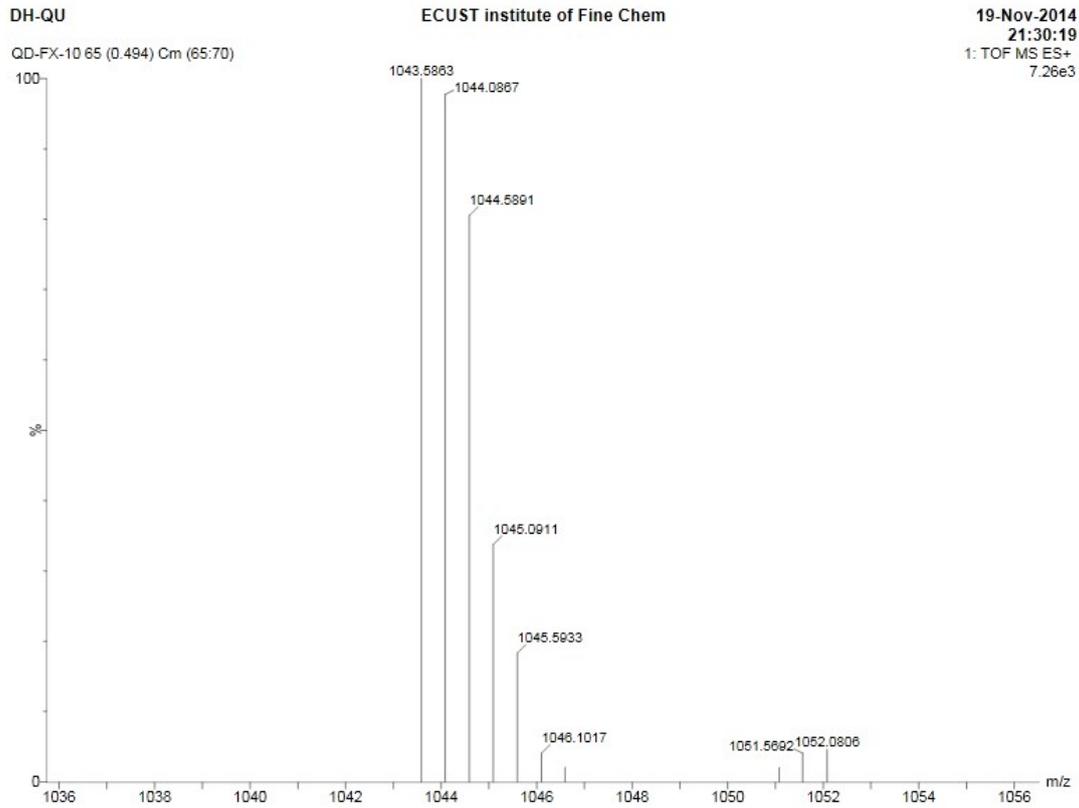
ESI-Mass spectrum of CP-Upy 10



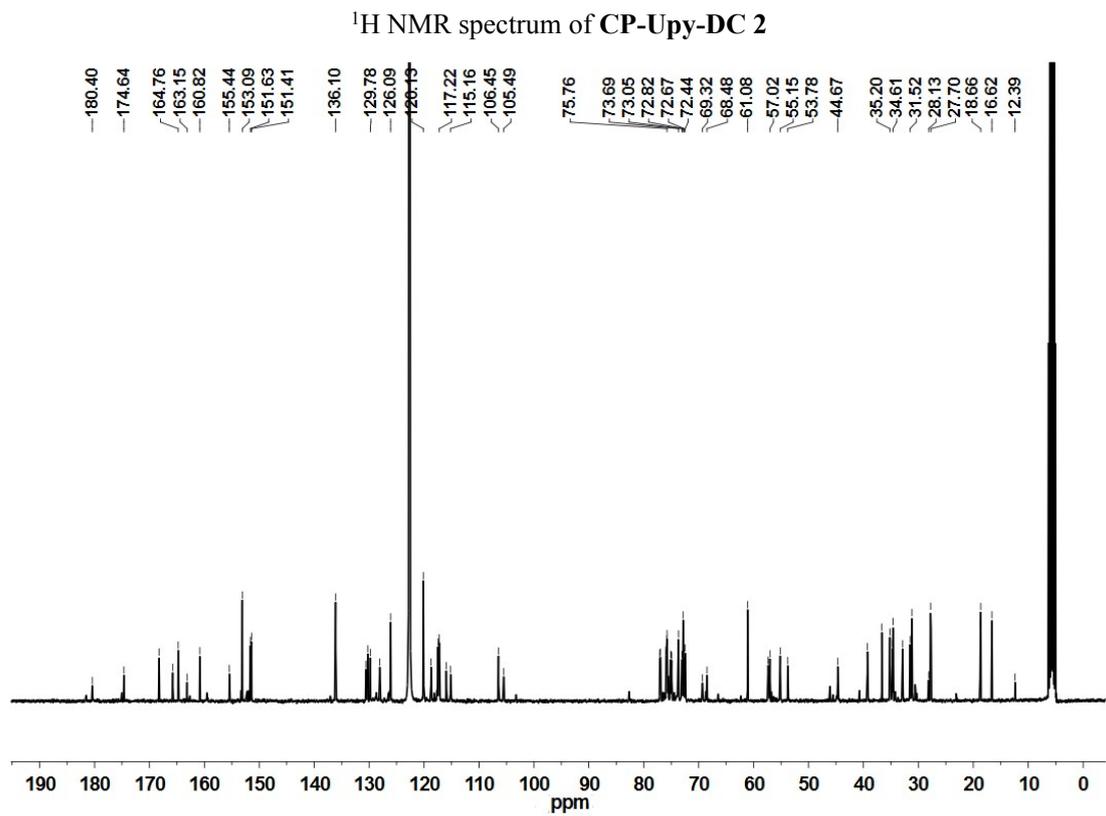
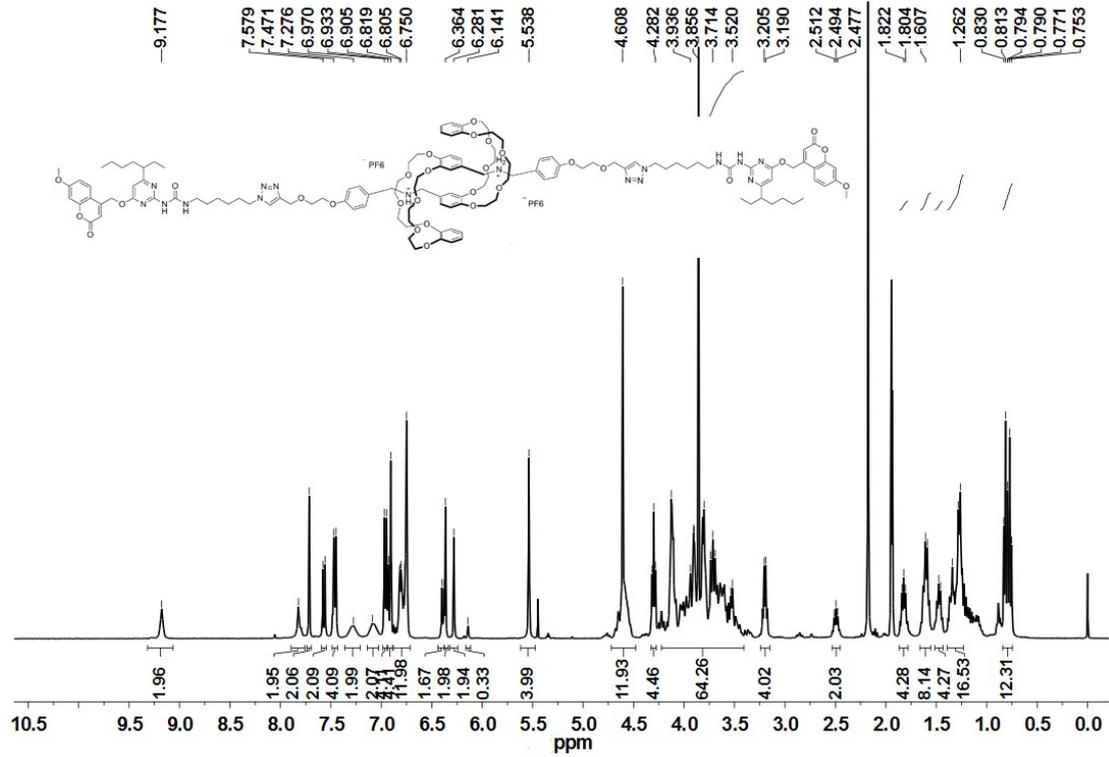
<sup>1</sup>H NMR spectrum of Upy-DC 1

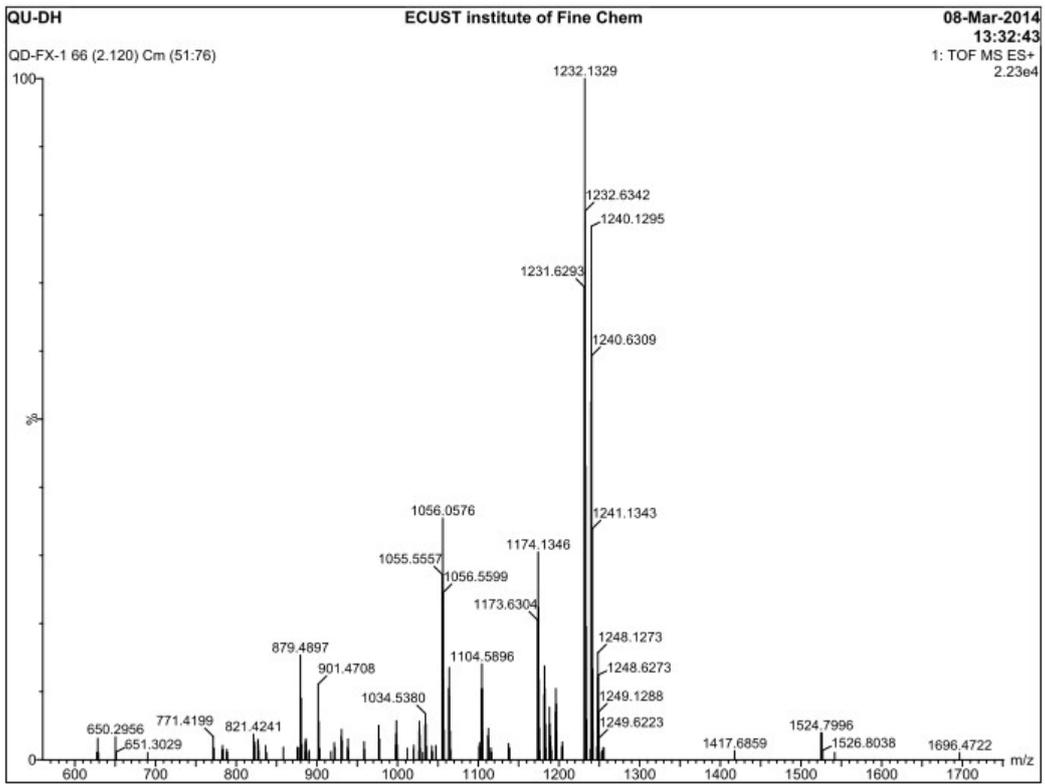


$^{13}\text{C}$  NMR spectrum of Upy-DC 1



ESI-Mass spectrum of Upy-DC 1





ESI-Mass spectrum of CP-Upy-DC 2